There is also the possibility of diffusion of molecules through the crystal lattice supporting the effect observed in dielectric study by Kiryama *et al* (1954).

On performing the experiment again at the room temperature, after heating the sample to about 475°K, the liquid line on the top of the solid line became more sharp, which is attributed as due to the diffusion of water molecules through the lattice. Evidence of this fact is obtained by X-ray investigations by Nitta and Watanabe (1937), and thermal studies by Nitta *et al* (1950).

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NUCLEAR MAGNETIC RESONANCE OF PHOSPHORUS NUCLEI

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The present note reports the effect of temperature on the n.m.r. line width of polycrystalline phosphorus pentachloride. It has been found that the PCl_4^+ and PCl_6^- lines are as suspected motionally narrowed at room temperature and that on cooling the motion freezes out giving broader lines. The lines overlap at 199°K.

The nuclear magnetic resonance spectrum of a solid is much broader than that of a liquid because of the static dipolar interaction between the nuclei in the solid. The isotopic re-orientation and diffusion of the molecules average their nuclear dipolar interaction almost to zero, which might then reveal a fine structure

due to the different chemical shifts of the nuclei and from their indirect spin-spin interactions. This fine structure is not revealed in solids because of stronger dipolar interactions. It has been shown (Andrew *et al* 1958, 1959 and Andrew 1959) that dipolar broadening of the nuclear magnetic resonance spectrum of a solid may effectively be removed by rotating the sample at a high speed about an axis inclined at an angle 54°44′ to the direction of the field. When the rotation rate is comparable with the static line-width the narrowed central line is resolved from the satellite lines, which appear on either side of it at integral multiples of the rotation frequency. Using this technique a doublet fine structure has been observed from polycrystalline phosphorus pentachloride. The phosphorus $-31(31_p)$ resonance spectrum is shown in figure 1. The sample was placed in an air tight container which was rotated about an axis making an angle of 54°44′ with the steady magnetic field of about 4740 oersteds. The side bands were scarcely distinguishable from the noise background, and the central spectrum consisted of two sharp lines of about equal intensity. It has been found in X-ray diffraction study (Clark *et al* 1942) that phosphorus pentachloride

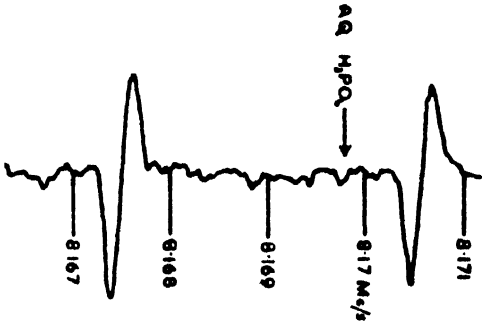

Figure 1. The Phosphorus—$31(31_p)$ resonance spectrum.

in the solid state consists of equal numbers of tetrahedral $(PCl_4)^+$ and octahedral $(PCl_6)^-$ ions packed in a tetragonal lattice. The two lines have been attributed to the different chemical shifts in the $(PCl_4)^+$ and $(PCl_6)^-$ ions of which the solid is composed. The spectrum has also been recorded in a field of about 3550 oersteds. It has been found that the line separation is proportional to the field strength as the chemical shift explanation requires.

Andrew *et al* (1962) have found that at room temperature the values of T_1 are approximately 6 sec. and 0.6 sec. for the tetrachloride and hexachloride ions, respectively. It was also observed that when the rate of rotation accurately coincides with the frequency interval between the two resonance lines, the two relaxation times become equal; the phosphorus nuclei in both types of ion then relax with the shorter time. This has been described as the nuclear cross-relaxation induced by rotation of the specimen.

The NMR broad line spectrometer used in the present investigation has been described elsewhere (Gupta 1963). For the detection of the resonance from the 31_p nuclei, the radio frequency bridge of the proton magnetic resonance spectrometer was slightly modified; the resonance frequency in a field of 6164 oersteds is 10.63 mcps. Due to the corrosive nature of the PCl_5, a special sample holder and can had to be made for this experiment. Besides liquid air, solid carbon dioxide was used for lowering the temperature of the specimen.

It has been assumed in our calcuations that the lines are gaussian and remain Gaussian after broadening.

When the polycrystalline phosphorus pentachloride was cooled; the ionic motion froze out and the lines started broadening as the temperature was lowered; the lines overlapped at about 199°K. The variation of line width with temperature is shown in figure 2. The inadequate signal to noise ratio did not warrant further study of the spectra. It was not possible to make any quantitative deductions except that the PCl_6^- line increases by about 0.75×10^{-2} gauss/°K and PCl_4^+ resonance line by 1.78×10^{-2} gauss/°K.

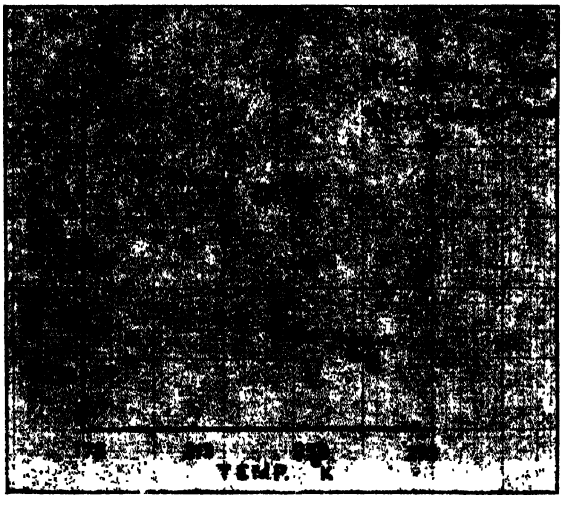

Figure 2. Variation of line width with temperature.

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